

Optimization of Methanol Synthesis from Carbon Dioxide and Hydrogen: Demonstration of a Pilot-Scale Carbon-Neutral Synthetic Fuels Process

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A pilot-scale reactor system was developed in order to demonstrate the feasibility of producing a carbon-neutral synthetic fuel from carbon dioxide and hydrogen gases. A pilot-scale, catalytic fixed bed reactor system was constructed to produce methanol and was evaluated for performance under a variety of experimental conditions. Reactor output was measured gravimetrically as a function of temperature, pressure, and space velocity in order to determine the most efficient and practical conditions for producing methanol. Reactor performance was quantified in terms of molar carbon conversion, selectivity, and space–time yield. Of the conditions studied, it was found that optimum wt % yield and carbon conversion of 49% and 14.3%, respectively, was achieved at 240 °C, 1800 psi, and gas hourly space velocity of 3300 h^{−1}. When considering limitations of equipment and apparatus, however, a more practical operating pressure would likely be 1400 psi, which resulted in a single-pass carbon conversion of 9.7% and a 44% yield of methanol by weight.

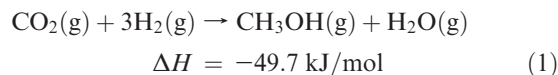
Introduction

Society has begun to demand the transition to a sustainable fuels economy. Sustainable energy sources such as wind, solar, and hydro are often touted as a solution to the energy crisis. There are many reasons why: they are renewable, domestic, cost-effective, pollution free, and their usage evolves no CO₂ emissions. However, these alternatives generate electricity only and do nothing to curb the demand and importation of petroleum, which is used primarily for transportation in the form of gasoline and diesel fuel. What is needed is a liquid transportation fuel that can be derived from renewable electricity and that can be shipped, stored, and seamlessly integrated into the current infrastructure. To this end, alcohol fuels such as methanol and ethanol are being pursued as a viable option for providing much needed energy to the transportation sector.

An ideal industrial process would be the formation of alcohols from atmospheric CO₂ and from H₂ generated by renewable electricity. This scheme may soon be realized as carbon capture technologies are beginning to emerge,¹ as are large-scale wind-to-hydrogen projects.² Capturing carbon dioxide from the atmosphere (or intercepting it before it reaches the atmosphere) and generating hydrogen from the electrolysis of water would provide both a fuel solution for market as well as a carbon cycling mechanism to combat the effects of global warming. It is the author's opinion that a carbon-neutral synthetic fuel, derived from renewable energy, is indeed an effective combat strategy for reducing the impacts of CO₂ in the atmosphere. Since no new carbon is added

during the production and utilization of such fuels, there is no net contribution to global warming.

Synthesis of methanol from CO₂ and H₂ has been known and practiced since at least 1930 and is a promising route to sustainability due to the potentially large demand for methanol as both a fuel and a basic chemical.^{3–6}



Here, we describe the optimization of reaction 1 as a demonstration of feasibility for the sustainable production of methanol. Carried out in a mini-pilot-scale, fixed bed, catalytic reactor system, CO₂ and H₂ react in the presence of a commercially obtained Cu/Zn catalyst to produce methanol and water. A single-pass, isothermal reactor system was constructed in order to measure the yield of methanol as a function of temperature (*T*), pressure (*P*), gas hourly space velocity (GHSV), as well as to evaluate the overall potential of the system as a commercial process.

The carbon conversion efficiency of the reaction was determined gravimetrically by simple distillation of liquid products, while the selectivity for methanol (vs other liquid products) and purity of methanol was determined by FT-IR spectroscopy and capillary gas chromatography. Results obtained here were in good agreement with those of other authors who were studying a similar system, with major differences being reactor size and catalyst load. Our review of the literature revealed only microscale, analytical reactor systems utilizing CO₂ as the sole carbon source. Systems

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explored by Lee, Lee, and Arakawa^{7–9} were ~100 to 10 000 times smaller than that presented here (0.01–1 g catalyst) and utilized custom-made catalysts. In contrast, our system utilized 60–100 g of commercially available catalyst and was evaluated for conversion efficiency at the pilot scale. Specht presents a comparable reactor size and catalyst load but provides little analytical data regarding performance of the system.¹⁰

Experimental Section

Unless otherwise noted, all pressure units are pounds per square inch (psi), all GHSV units are liters synthesis gas per liter catalyst per hour ($L_{\text{syngas}} L_{\text{cat}}^{-1} \text{h}^{-1}$, also abbreviated as h^{-1}), and temperature units are in degrees Celsius ($^{\circ}\text{C}$). The commercial catalyst used in this study, Katalco 51–8, was donated by Johnson Matthey, Inc. The $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst was received as solid cylindrical pellets with a packing density of $1190 \text{ kg}/\text{m}^3$.¹¹ Synthesis gas was premixed at 75 mol % H_2 and 25 mol % CO_2 and was obtained locally from Praxair, Inc. The cylindrical reactor was constructed in-house from 316SS with 12 in. length and an internal diameter of 1 in. All pressurized gas lines were 316SS 0.25 in. o.d. tubing and sealed with Swagelok fittings. Gas flow rates were regulated using Brooks 5850 mass flow controllers, which were calibrated with a certified mass flow meter from Alicat Scientific. Reactor pressure was maintained by a back pressure regulator monitored via a pressure transducer with digital display. The reactor temperature was maintained by an external, electrical heating block and a PID temperature controller. The catalyst bed temperature was measured during reactions using a type K thermocouple positioned within the reactor itself, near the center of the catalyst bed. Figure 1 shows a schematic of the reactor system described here.

For all experiments, 0.1 L of catalyst was loaded as received into the reactor and was reduced at 180°C , 100 psi, and 500 h^{-1} for 24 h in an atmosphere of 2% H_2 and 98% N_2 .¹¹ The reactor was then flushed with H_2 for 1 h before introducing the synthesis gas. Experiments were performed by establishing T , P , and GHSV conditions followed by a 15 min equilibration time to achieve steady state. Reaction products were collected for 20 min of continuous synthesis. Experimental conditions are summarized in Table 1, and all data is represented as the average of triplicate measurements, unless otherwise noted.

Synthesis products were purified by simple distillation to determine conversion efficiency, reported as molar CO_2 conversion and space–time yield (STY). Sample distillates were first analyzed by FT-IR to confirm methanol as the major product, then by capillary gas chromatography to identify and to quantify any byproducts that may be present in the finished sample. The FT-IR was a Varian Excalibur 3100 with a single bounce Pike ATR accessory. The two gas chromatographs used for purity analysis were a Varian Saturn 2100T for identification of byproducts by mass spectrometry and a Shimadzu GC-14A with a flame ionization detector for quantification of byproducts. In addition, the reactor exhaust stream was analyzed by FT-IR spectroscopy to determine the amount of carbon monoxide (CO) that was formed.¹² Since only a fraction of the synthesis gas is consumed upon a single pass through the reactor, effective

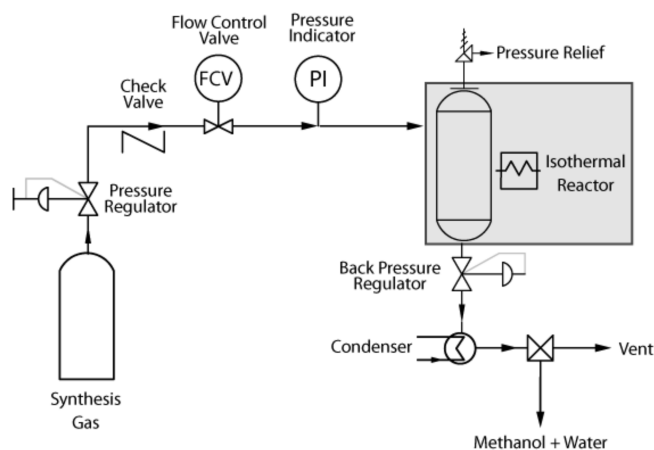


Figure 1. Schematic diagram of the single-pass methanol synthesis apparatus.

Table 1. Experimental Conditions for Methanol Synthesis

catalyst load (kg)	particle size	pressure (psi)	temperature ($^{\circ}\text{C}$)	space velocity ($\text{L}/\text{L}_{\text{cat}}/\text{h}$)
0.06	Full	1000–1400	220–260	10 000
0.10	Full	1000–1800	240	3300–8300
0.10	16/30 mesh	1000–1800	240	3300–8300

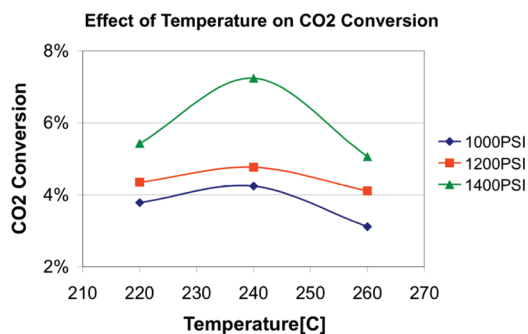


Figure 2. CO_2 conversion to methanol as a function of temperature and pressure at $\text{GHSV} = 10\,000 \text{ h}^{-1}$.

commercialization of the process described here will require gas recirculation so that high conversion efficiencies can be realized. Thus, the composition of exhaust gas is an important parameter for optimization of a more advanced reactor system.

Results and Discussion

I. Methanol Yield and Conversion Analysis. Reactor productivity was evaluated by CO_2 conversion (mol $\text{MeOH}/\text{mol CO}_2$) and STY ($\text{kg}_{\text{MeOH}}/\text{L}_{\text{cat}}/\text{h}$). The first suite of experiments was performed in order to determine the optimum temperature for methanol synthesis. For these experiments, GHSV was held constant at $10\,000 \text{ h}^{-1}$; temperature was fixed at either 220, 240, or 260°C ; and pressure was varied from 1000 to 1400 psi. Summarized in Figure 2, the results show little effect of temperature on methanol yield for the 1000 and 1200 psi data sets. However, at 1400 psi there is a maximum methanol yield at 240°C , this was therefore chosen as the set point reaction temperature for all subsequent experiments. There are no error bars in Figure 2 as this data set was not taken in triplicate.

The second suite of experiments was conducted in order to observe the effects of pressure and space velocity on CO_2 conversion and STY. As mentioned above, the reactor

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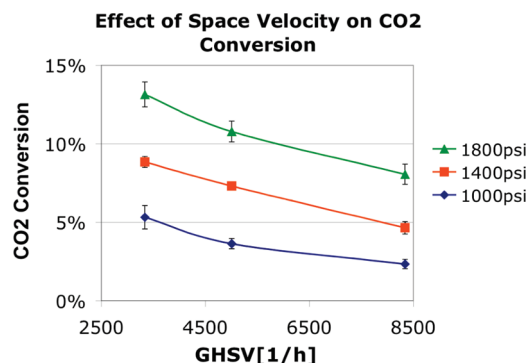


Figure 3. CO₂ conversion as a function of space velocity and pressure, $T = 240\text{ }^{\circ}\text{C}$.

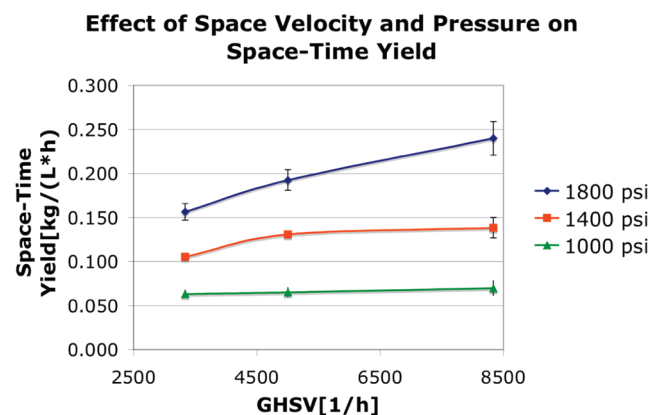


Figure 4. Space-time yield (STY) as a function of pressure and space velocity, $T = 240\text{ }^{\circ}\text{C}$.

temperature was set to $240\text{ }^{\circ}\text{C}$. Pressures of 1000, 1400, and 1800 psi were explored at GHSV values of 8300, 5000, and 3300 h^{-1} . Figure 3 summarizes the results, which show a monotonic decrease in CO₂ conversion with increasing GHSV and a sharp increase with pressure up to 1800 psi.

II. Methanol Purity and Byproduct Analysis. Following confirmation by FT-IR, the synthesized methanol was analyzed for purity and presence of byproducts by capillary gas chromatography. Following simple distillation, $1.0\text{ }\mu\text{L}$ of product methanol was injected onto a DB-5 GC column. Comparison was made to reagent grade methanol (Fisher Scientific) and to a calibration solution made of reagent methanol spiked with 0.01% (v/v) each of ethanol, isopropanol, isopentanol, and 0.05% (v/v) 1-butanol as an internal standard. For quantitative analysis, the synthetic methanol was also spiked with 0.05% (v/v) 1-butanol as an internal standard prior to injection.

Representative chromatograms (Figure 5) show the presence of 6 minor byproducts in the distillate methanol that, after quantification, represent a total concentration less than 0.05% (v/v). On the basis of retention time correlations with the calibration standards and library search results using NIST MS Search 2.0, the trace impurities were identified as ethanol, isopropanol, 1-propanol, 2-butanol, 1-butanol, and 2-methyl-1-propanol, all of which are acceptable byproducts that should have little or no effect on combustion properties or engine performance when used in modern vehicles.

Results of exhaust gas measurements by FT-IR¹² are summarized in Table 2. Measured at 1400 psi, it was found that carbon monoxide is a major component of the exhaust

Methanol Purity Analysis by GC-FID Representative Chromatograms

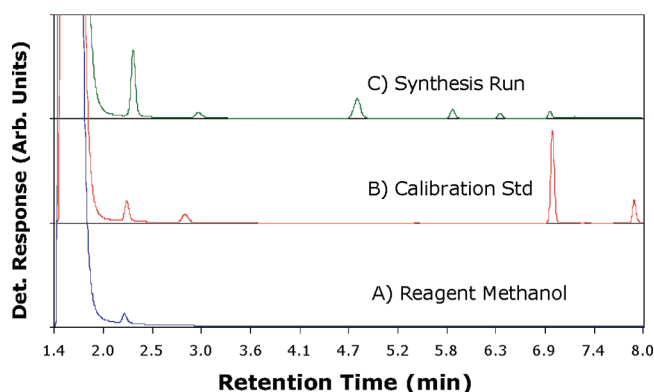


Figure 5. (A) Reagent grade methanol; (B) Calibration solution made from 0.01% (v/v) ethanol (RT = 2.2 min), isopropanol (RT = 2.9 min), isopentanol (RT = 7.9 min), and 0.05% (v/v) 1-butanol (RT = 6.9 min); (C) Synthetic methanol produced at 1400 psi and 4500 h^{-1} (enlarged to show detail).

Table 2. Selected Results for Methanol Synthesis Characterization

pressure (psi)	GHSV (h^{-1})	yield (wt %)	H ₂ conv. ^a (mol %)	CO ₂ conv. ^b (mol %)	CO (mol %)	byproducts (vol %)
1000	3300	33.8 ± 3.6	1.8 ± 0.3	5.81 ± 0.8		
	5000	31.5 ± 1.1	1.3 ± 0.1	3.97 ± 0.3		
	8300	25.9 ± 1.0	0.9 ± 0.1	2.56 ± 0.3		
1400	3300	43.7 ± 0.3	3.2 ± 0.1	9.7 ± 0.4	7.9	
	5000	41.1 ± 0.8	2.7 ± 0.1	8.0 ± 0.2	12.7	0.017
	8300	34.5 ± 0.9	1.7 ± 0.1	5.1 ± 0.4		
1800	3300	49.0 ± 0.9	4.8 ± 0.3	14.3 ± 0.9		
	5000	45.6 ± 1.6	3.9 ± 0.2	11.8 ± 0.7		0.032
	8300	41.0 ± 2.2	2.9 ± 0.2	8.8 ± 0.7		

^a H₂ conversion calculated as molar ratio of methanol produced to total H₂ flow through reactor. ^b CO₂ conversion calculated as molar ratio of methanol produced to total CO₂ flow through reactor.

stream having a total molar concentration of 7.9% at 5000 h^{-1} and 12.7% at 3300 h^{-1} .

Overall, the results obtained were promising with respect to scale-up and commercial implementation of the process described here. Methanol yields were higher than those reported elsewhere, but this is most probably attributed to higher operating pressures; 1400–1800 psi in this study versus ~ 400 psi in the literature cited here. CO₂ conversion and STY are comparable to literature values; wt % yield was quite high, as much as 43% on a carbon basis; byproducts in the finished methanol were exceptionally low, less than 0.05% by volume; exhaust gas analysis reveals a carbon monoxide level between 8 and 13% on a molar basis. Quantitative comparison of reactor research can be difficult due to the many possible differences in reactor design. However, qualitative agreement can still be useful for affirming theoretical assertions. For instance, the data collected by Arakawa et al.⁷ is in concordance with our understanding that wt % yield increases with decreasing space velocity. Our research also agrees with the Arakawa research in the understanding that methanol yield increases continually with pressure.

The important conclusion of Lee et al. is that carbon dioxide hydrogenation is faster than carbon monoxide hydrogenation and thus should be considered the primary source of carbon in methanol synthesis.⁹ This, as well as work by Specht and Bandi,¹⁰ bolsters the intent to

repurpose carbon dioxide as the basis of the methanol economy.⁶

Future work will include a 10× scale up and the implementation of a gas recycle system so the exhaust stream can be continuously fed into the reactor, thus achieving high conversion efficiencies. Experiments will be conducted in order to evaluate the long-term performance of the catalyst, and the catalyst will be analyzed for coking (carbon build-up) by scanning electron microscopy. Additional analytical methods will include in situ gas chromatography and FT-IR measurements of single-pass and recycled exhaust gas

streams for hydrogen, methane, and carbon monoxide content. Finally, a CO₂ capture system will be constructed for implementation at a local microbrewery in order to demonstrate the feasibility of carbon capture and subsequent conversion to methanol.

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